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| 13. ABSTRACT (Maximum 200 words) Mesoporous intercalation electrode materials were prepared, characterized, and their electrochemical performance evaluated. The usual characterization techniques were complemented by our (novel!) use of electron microprobe analysis to examine the homogeneity of the products. The results show that in many cases, oxidation/reduction does not significantly alter the local structure about the electroactive metal ions in these relatively open structures, thus increasing the electrochemical reversibility. These structures also appear to facilitate ionic diffusion. Well-ordered mesoporous SnO and SnO ₂ were successfully prepared and exhibited higher specific capacities than the carbon materials presently used in the anodes of lithium ion batteries. These materials clearly have potential application as intercalation anode materials. The cycling behavior of manganese and vanadium substituted into a mesoporous host aluminophosphate framework showed very good reversibility, while rate capacity studies indicated excellent capacity retention. It is clear that the open mesoporous host structures facilitate the transport of lithium ions through the framework. The University provided funds to purchase an x-ray system in support of this work, with the provision that it be shared with other scientists on campus. Although no ARO funds were used for the purchase, the grant support from ARO played a major role in this acquisition. | | | |
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FINAL PROGRESS REPORT

1. Foreword

This final progress report summarizes the work accomplished and the results obtained under ARO grant number DAAH55-98-1-0252. Although several significant milestones were accomplished as described below in Section 5, in several ways this project proved to be rather frustrating. The solid state syntheses necessary to obtain the desired products were delicate and complex, and for at least a year we were misled about the nature of our final products by the usual characterization techniques found in the literature: transmission electron microscopy, X-ray diffraction analysis, and BET isotherm measurements. As detailed below, the eventual (and novel!) use of electron microprobe analysis finally allowed us to examine the homogeneity of our mesostructural materials at an appropriate resolution. However, the results of numerous syntheses then had to be rejected because the products were heterogenous, consisting of the desired substituted mesoporous materials as a minority phase intermingled with several dense, amorphous phases.

It is particularly noteworthy that one of our papers* was featured in the recent Tech Highlights section of Interface**, a newsletter published by the Electrochemical Society

*[Novel High Rate Lithium Intercalation Materials", *J. Electrochem. Soc.* **149**, A99-A102 (2002)].

***Interface* 11(2), 27 (2002).

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4. Statement of Problem Studied

The research problem was to prepare intercalation cathodes (and anodes) which are mesostructural or mesoporous in nature, using a variety of synthetic routes. Mesoporous materials are three-dimensional crystalline framework structures consisting of an inorganic wall and a regular, well-defined channel system with pore sizes between 2 and 50 nm. Our motivation was based on the fact that irreversible structural modifications play a major role in the capacity loss of electrode materials over extended cycling. We anticipated that oxidation/reduction would not significantly alter the local structure about the transition metal ions during charge and discharge in these relatively open structures, thus increasing the electrochemical reversibility. These materials would also have high specific areas, thereby increasing the practical electrochemical capacity. In addition, we anticipated that the presence of open site-to-site channels of large dimension would increase the ionic diffusion through the cathode host material.

After preparation, the mesoporous materials were structurally characterized with low angle powder X-ray diffraction, electron microscopy, and *in situ* vibrational spectroscopic techniques. Composite electrodes were then prepared and their electrochemical performance evaluated in lithium rechargeable batteries, with particular attention to the capacity and capacity loss over a large number of cycles (cyclability). These data were then compared to analogous data with electrode materials obtained from solid state reaction and solution routes.

5. Summary of Most Important Results

M-substituted, silicate-based mesophases (M=Co, Sn, Mn). Our efforts initially focused on three systems: cobalt-substituted aluminosilicate mesophases, tin-substituted silicate mesophases, and manganese-substituted silicate mesophases. The initial electrochemical characterization of these materials was quite promising. However we experimented with electron microprobe analysis to examine the elemental composition of our samples and quickly found that the high spatial resolution of the technique allowed us to examine sample homogeneity at a micron or submicron scale. We then discovered that our Mn-substituted mesophases were highly heterogeneous when the substitution levels were above 2% Mn. Therefore we reluctantly concluded that the capacity and cycling data were suspect, because it was not possible to separate the contributions to the electrochemical activity from the Mn-substituted mesophase and the Mn-containing, highly amorphous phases. This unfortunate finding required us to withdraw a manuscript submitted to and accepted by the Journal of Power Sources for publication as a full paper. Following up on the use of electron microprobe analysis to examine sample composition, we also confirmed that the cobalt-substituted aluminosilicate mesophases and tin-substituted silicate mesophases were significantly heterogeneous at any significant levels of substitution.

Conclusions: Synthesis of mesoporous materials mediated by directing agents followed by calcination to remove the template can produce heterogeneous materials, often accompanied by the partial or total collapse of the mesostructure. Although the resulting product may appear to yield high initial discharge capacities, the capacity fade in such systems is very rapid. The use of electron microprobe analysis provides an invaluable check on the homogeneity of the product.

Pure mesoporous SnO and SnO₂. We synthesized pure mesoporous SnO and SnO₂ to see if these compounds afforded any advantages over carbon-based intercalation anodes. Since it is extremely difficult to prepare a Sn-O inorganic network using cationic or neutral surfactants as templating molecules we chose the anionic surfactant sodium dioctylsulfosuccinate (AOT). Because the tin ions tend to polymerize in solution to form a Sn-O network between pH 4 and pH 8.5, we found that pH control is critical in the templating synthesis. TEM pictures of both SnO and SnO₂ samples indicated that the products formed hexagonal mesoporous phases with a pore spacing of about 5 nm. After calcination, the mesoporous structure was retained but the pore diameters decreased to about 3 nm.

Composite electrodes prepared with the mesoporous structures were cycled at a constant current density of 0.1 mA/cm² (equivalent to a c/12 rate). The cutoff voltages were from 0 to 1.4 V vs. Li/Li⁺. The cycling profiles were similar to those of the powdered tin oxide reported in the literature. The details of the initial charge-discharge data are given in Table 1. The initial capacity loss of SnO₂ was of 520 mAh/g, which was about 48% of the first discharge capacity. The capacity loss for SnO calcined in air was 414 mAh/g and for SnO calcined in N₂, 355 mAh/g. The capacity loss data for SnO calcined in air are shown in Figure 1 in the Appendix. The discharge behavior of

mesoporous SnO₂ and SnO calcined at air was quite similar, which might be due to the formation of SnO₂ when SnO is calcined at 500 °C. The cycling behavior of the electrodes shows very good reversibility, e.g. for SnO calcined in air the charge capacity during the 5th cycle was still 450 mAh/g. Among these samples, SnO calcined in N₂ gave least capacity loss and SnO₂ showed best reversibility. These cycling data are shown in Figure 2 in the Appendix.

Conclusions: Well-ordered mesoporous SnO and SnO₂ can be prepared using a templating synthesis with AOT as the surfactant. Electrochemical tests showed that the mesoporous materials gave better electrochemical performance in terms of specific capacity and cycling behavior than crystalline SnO and SnO₂. All of the samples exhibited higher specific capacities than the carbon materials presently used in the anodes of lithium ion batteries. These materials clearly have potential application as intercalation anode materials.

Mesoporous Sn-P-Si materials. Modification of a host silicate mesostructure with phosphorous allowed the substitution of Sn at reasonably high levels, yielding a mesoporous material with an average pore size of about 4 nm after calcination. Two calcination atmospheres, N₂ and air, were used during these experiments. The N₂ atmosphere was chosen to maintain Sn²⁺ oxidation state while the air calcination atmosphere was utilized to oxidize Sn²⁺ to Sn⁴⁺.

Composite anodes were prepared with these materials and cycled over a voltage range of 0-1.4 V versus Li/Li⁺ at current densities of 0.1, 0.2, and 0.5 mA/cm² which are equivalent to c/8, c/4 and c/2 rates, respectively. The initial charge-discharge data for several Sn-Si-P-O systems are shown in Table 2 in the Appendix. The initial charge capacities of these materials ranged from 370 to 450 mAh/g. These charge capacities are smaller than those of pure tin oxide because the electrochemically active tin is partially replaced by the non-electrochemically active elements P and Si to form the framework walls of the mesoporous structure. The irreversibility of these materials was almost the same as that noted for the mesoporous tin oxides (≈50%) as previously discussed. The rate capability showed very good capacity retention; for the Si-P-Sn-O sample (Sn: P: Si=1:1:1, calcined in air) the capacity was over 312 mAh/g at a discharge current density of 0.5 mA/cm². The longer term cycling behavior was acceptable with the Si-P-Sn-O material (Sn: P: Si=1:1:1, calcined in air) exhibiting a capacity over 275 mAh/g on the 100th cycle. We speculate that the reason for the better reversibility compared to that of the pure SnO compound is that the additional Si-P-O linkages provide an amorphous network to support LiSn alloy formation during discharge and SnO formation during charge.

Conclusions: A novel templating synthesis (using two surfactants!) can be used to prepare a well-ordered Sn-Si-P-O mesophase with a pore spacing of 4 nm. The mesophase exhibits very good specific capacity and reversibility. Mesoporous electrode materials provide efficient pathways for lithium intercalation by increasing the chemical diffusion coefficient of lithium in the matrix. With increasing levels of Sn substitution in the Si-P-O matrix, both the charge capacity and the irreversibility increased, although

there is an upper limit to the amount of Sn that can be substituted and still retain the mesoporous structure of the electrode material.

Mn- and V-substituted, Al-P-O mesoporous materials. A mesoporous material with an average pore size of about 4 nm was prepared with manganese substituted into a host aluminophosphate (Al-P-O) framework using cetyltrimethylammonium bromide (CTAB) as the structure-directing agent. Electron microprobe analysis established that the samples were homogenous even with a Mn:Al:P composition of 1:1.27:1.76. The average discharge voltage of the Mn-Al-P-O material was approximately 2.9 V at a constant current density of 0.2 mA cm^{-2} . The cycling behavior of both Mn- and V-containing matrices showed very good reversibility at this current density. The initial discharge capacity of the Mn-Al-P-O material decreased only 3% by the 80th cycle. These data are illustrated in Figure 3 in the Appendix.

Rate capacity studies of both Mn- and V-substituted materials indicated very good capacity retention. The 3rd discharge capacity of the Mn-Al-P-O matrix (nominal Mn:Al:P=1:1:1) cycled at 2 mA cm^{-2} (approximately a 3C rate) was 75% of the discharge capacity when the electrode cycled at 0.1 mA cm^{-2} . The analogous value for the V-Al-P-O matrix (V:Al:P=1:1:1) was about 65 %. These data are shown in Figure 4 of the Appendix.

Conclusions: A mesoporous framework can be prepared that is robust with respect to rapid intercalation/deintercalation of lithium ions. These open structures appear to facilitate the transport of lithium ions in the electrode material. Unfortunately, the specific capacity remains a serious problem. In the Mn-Al-P-O matrix, the initial discharge capacity is 51 mAh g^{-1} ; the corresponding value for the V-Al-P-O matrix is 82 mAh g^{-1} . In spite of the dramatic capacity retention at high discharge rates, the specific capacities of these materials are as yet too low to be considered for commercial applications.

In-situ spectroscopic measurements of lithium insertion. *In situ* Raman spectra of spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ ($x=1.0$ and 1.1) were collected through the 80X objective of a microscope in a backscattering geometry during electrochemical intercalation of lithium ions. The spectra of stoichiometric LiMn_2O_4 were measured over the first charge and discharge curve in the potential range of 4.60 to 2.85 V vs. Li/Li^+ . This study indicated that a single-phase reaction is followed by a two-phase reaction and then by another single phase reaction when lithium is deintercalated from the spinel compound ($0.1 < x < 1$). In nonstoichiometric $\text{Li}_x\text{Mn}_2\text{O}_4$ ($x=1.1$), Raman spectra clearly identify the presence of the λ - MnO_2 phase in the cathode during charge and discharge. When spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ was intercalated with lithium ions, the *in situ* spectral changes were consistent with a two-phase reaction between the cubic and tetragonal phases.

Conclusions: These experiments demonstrated that global phase changes and more subtle structural modifications within a phase can be identified using *in situ* Raman spectroscopy. These results show that it would be highly desirable to develop methods of performing *in situ* infrared absorption measurements of intercalation processes in lithium

electrodes. In particular, it would be extremely useful to extend the spectral range to include the far infrared region ($400\text{-}30\text{ cm}^{-1}$).

Fe-substituted, Al-P-O mesoporous materials. We have successfully prepared an iron-substituted Al-P-O mesoporous material with a Fe:Al:P ratio of 0.153:0.862:1.000. The material is homogeneous under electron microprobe analysis. Low angle x-ray diffraction characterization showed an average pore spacing of 50.2 \AA . A series of x-ray photoelectron spectroscopic measurements indicated that iron was present as Fe(III) in an environment similar to that in Fe_2O_3 . Initial electrochemical measurements against lithium metal showed an open circuit voltage of 2.82 V .

Conclusion: Mesoporous Al-P-O can be prepared as a robust host for the substitution of a variety electrochemically active species, rather than being restricted to just manganese and vanadium as earlier efforts suggested.

Research infrastructure resulting from ARO support. During the second year of support, the University made funds available to purchase a x-ray system with small angle capability to confirm the mesoporous nature of our samples and to measure average pore sizes. We have purchased a Scintag X2 system and have extensively utilized it during the last two years of the grant. This system is shared between the Department of Physics and Astronomy and the Department of Chemistry and Biochemistry, providing a versatile capability for a number of users in both departments. Although no ARO funds were used for this purchase, the grant support from ARO for research in mesostructural materials was played a major role in this acquisition.

6. Listing of all publications and technical reports supported under this grant.

(a) Papers published in peer-reviewed journals.

i. W. Huang and R. Frech, "In Situ Raman Spectroscopic Studies of Electrochemical Intercalation in $\text{Li}_x\text{Mn}_2\text{O}_4$ -Based Cathodes," *J. Power Sources* **81-82**, 616-620 (1999).

ii. A. Yu and R. Frech, "Mesoporous Tin Oxides as Lithium Intercalation Anode Materials", *J. Power Sources* **104**, 97-100 (2002).

iii. A. Yu and R. Frech, "Novel High Rate Lithium Intercalation Materials", *J. Electrochem. Soc.* **149**, A99-A102 (2002).

iv. X. Zhang and R. Frech, "Manganese-Substituted Mesophase as Intercalation Cathodes in Lithium batteries," *J. Power Sources*.

(This last paper was accepted for publication and then subsequently withdrawn by me because electron microprobe studies showed that the manganese-substituted mesophases were very heterogeneous.)

(b). Papers published in non-peer-reviewed journals or in conference proceedings.

NA

(c). Papers presented at meetings

i. R. Frech and Weiwei Huang, "In Situ Raman Spectroscopic Studies of Electrochemical Intercalation in $\text{Li}_x\text{Mn}_2\text{O}_4$ - Based Cathodes", Ninth International Meeting on Lithium Batteries, July 12-17, 1998, Edinburgh, Scotland.

ii. R. Frech and Xulong Zhang "Manganese-Substituted Mesophases as Intercalation Cathodes in Lithium Batteries", Ninth International Meeting on Lithium Batteries, July 12-17, 1998, Edinburgh, Scotland.

iii. C. Rhodes, C. Burba and R. Frech, "Novel Cathode Materials for Sodium-Based Rechargeable Batteries," 43rd Annual Pentasectional Meeting, Oklahoma Sections of the American Chemical Society, August 15, 1998, Ponca City, OK.

iv. A. Yu and R. Frech, "Novel Sn-P-Si-O Materials as Anode Materials for Lithium Ion Batteries", 45th Pentasectional ACS Meeting, April 15, 2000, Stillwater, OK.

Table 1. Initial charge-discharge data for several Sn-O mesoporous materials

| Sample | 1st discharge (mAh/g) | 1st charge (mAh/g) | Irreversibility (irrev. capacity/discharge capacity) |
|----------------------------------|--------------------------|-----------------------|---|
| SnO ₂ | 1080 | 560 | 48% |
| SnO(calcined in air) | 1034 | 620 | 40% |
| SnO(calcined in N ₂) | 890 | 535 | 39% |

Table 2. Initial charge-discharge data for several Sn-Si-P-O systems.

| Sample | 1st discharge capacity (mAh/g) | 1st charge capacity (mAh/g) | Irreversibility |
|--|--------------------------------------|-----------------------------------|-----------------|
| Sn:P:Si=1:1:1(calcined in air) | 876 | 443 | 49.4% |
| Sn:P:Si=1:1:1(calcined in N ₂) | 735 | 370 | 49.6% |
| Sn:P:Si=2:1:1(calcined in air) | 957 | 545 | 43.1% |
| Sn:P:Si=2:1:1(calcined in N ₂) | 912 | 450 | 50.6% |

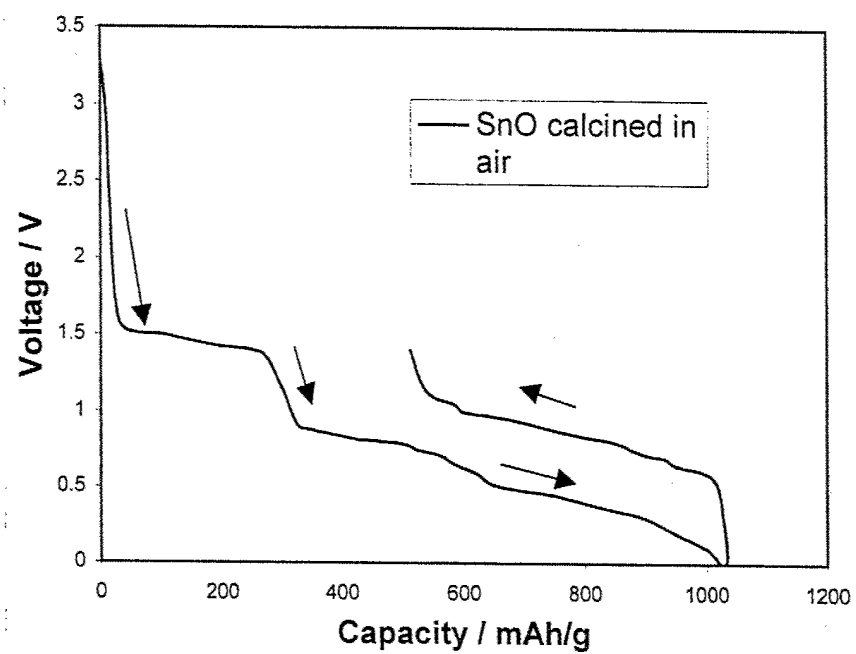


Figure 1

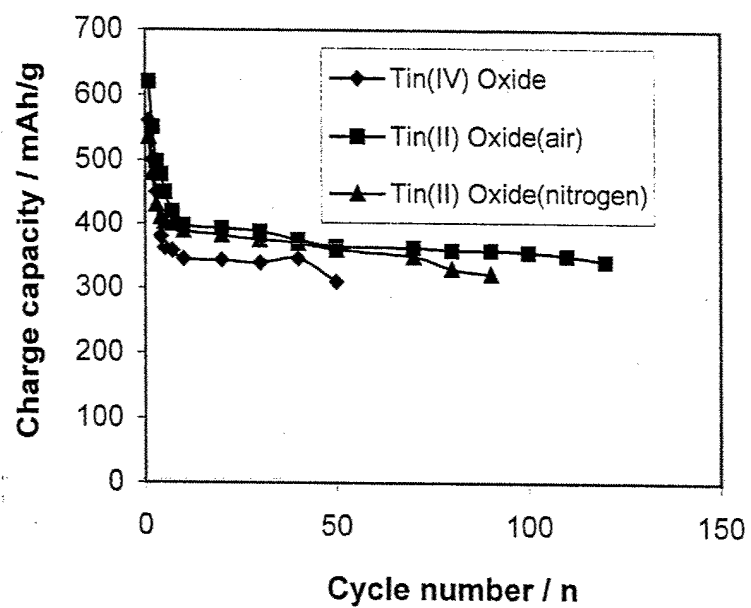


Figure 2

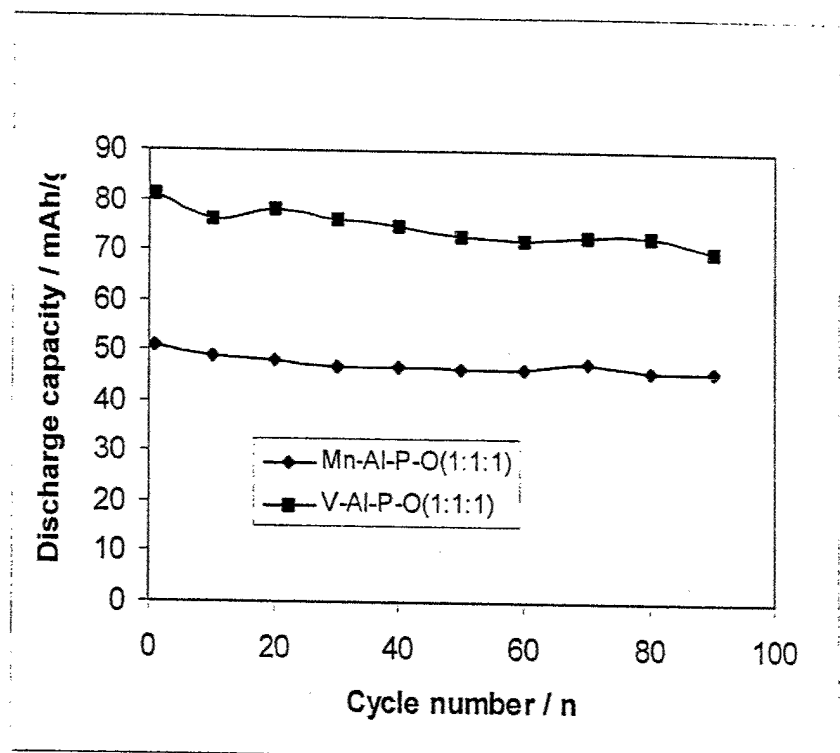


Figure 3

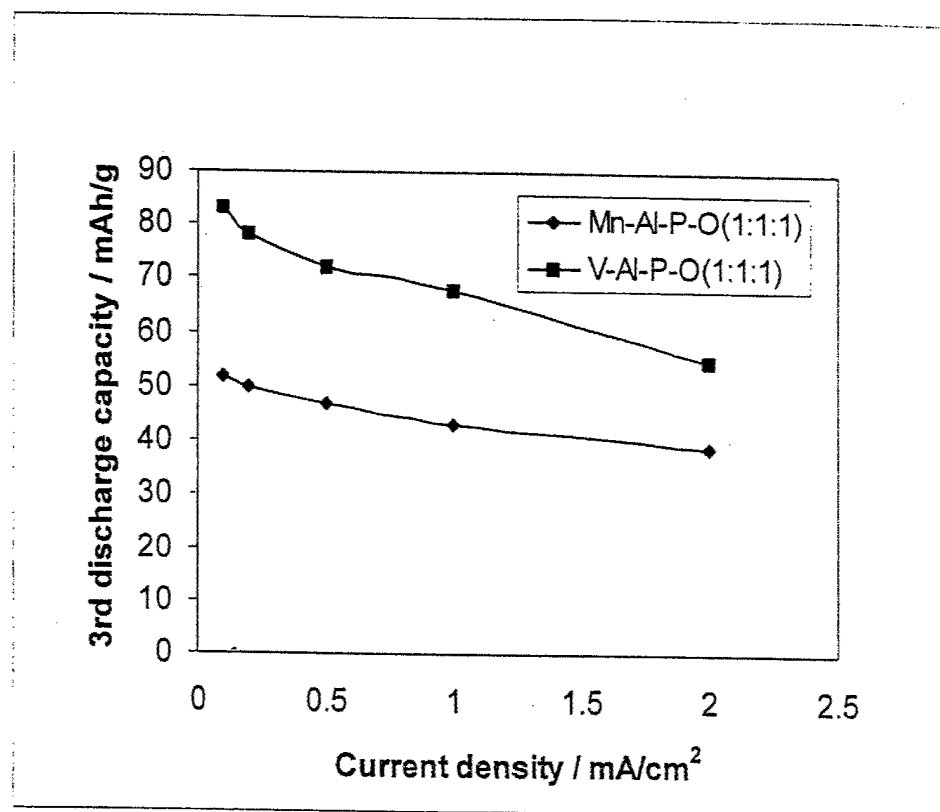


Figure 4

INTERFACE

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TECH HIGHLIGHTS

Novel Lithium Intercalation Cathode Materials

The development of secondary lithium batteries requires high performance electrode materials. Although crystalline metal oxides prepared by conventional solid-state reactions show reasonable specific capacities, electrode kinetics and the reversibility of their insertion reactions can still be improved. One of the strategies that has been employed to enhance cathode performance is decreasing the preparation temperature. These low temperature cathode materials are generally less crystalline, with more open structures and higher specific areas compared to the corresponding high temperature materials. As a further extension in this direction, researchers at the University of Oklahoma have investigated mesoporous materials based on an aluminum-phosphorous-oxygen framework containing both manganese and vanadium. The mesoporous structures are formed by the crystallization of gels organized by a surfactant templating agent. Electrochemical evaluation of these matrices as host cathode materials for lithium intercalation indicates that the materials exhibit very good rate capacity and reversibility under cycling. The results show that the mesoporous framework structures are robust with respect to lithium insertion and are thus viable candidates for development as high rate lithium battery cathode materials.

From: *J. Electrochem. Soc.*, 149, A99 (2002)

A Novel, High CO Tolerance Fuel Cell Electrocatalyst

Considerable effort has been expended at various research institutes to develop electrocatalysts for methanol fuel cells that are inexpensive and not prone to poisoning by carbon monoxide. Large-scale application of methanol polymer electrolyte membrane (PEM) fuel cells has been retarded by the lack of a suitable electrocatalyst. Researchers at Brookhaven National Laboratory in New York recently demonstrated a new fabrication method for Pt-Ru and other bimetallic electrocatalysts that results in lower Pt loading and increased resistance to CO poisoning compared to commercial Pt-Ru alloy electrocatalysts. Brankovic, Wang, and Adzic showed that Pt clusters could be spontaneously deposited on Ru nanoparticles via electrodeless deposition from a solution of hexachloroplatinic acid. Electrodes made using this technique were more than 3 times as active as a commercially available Pt-Ru electrocatalyst, as determined by comparison of their respective Pt-mass-specific oxidation currents. The authors believe that their deposition technique uses Pt more effectively by placing it only on the surface of Ru nanoparticles rather than throughout the bulk.

From: *Electrochem. and Solid-State Lett.*, 4, A217, (2001)

Decoration of Defects in Monocrystalline Silicon

Defects in device areas of silicon integrated circuits can be an important limiting factor in fabrication yields and device performance. As device feature sizes decrease in new generations of microelectronics, the demand on the quality of the silicon substrate becomes more stringent. Microdefects in state-of-the-art silicon are primarily self-interstitials (silicon atoms displaced from normal positions in the lattice) and vacancies (formed by missing atoms in the lattice). Researchers at MEMC Electronic Materials in Missouri have reported a detailed analysis of microdefect decoration techniques. They describe a multi-step procedure whereby they saturate the wafer with copper at 800°C, rapidly cool the wafer to nucleate copper on the microdefects and facilitate subsequent growth of precipitates, and then decorate the defects by chemical surface polishing and decoration etching (e.g., with the well-known Secco or Wright etchants). The authors developed

theoretical descriptions and phenomenological models that accurately describe the kinetics and thermodynamics of etch pit formation resulting from differences in etching rates of the precipitate-influenced region around a microdefect and the surrounding, defect-free silicon.

From: *J. Electrochem. Soc.*, 149, G153 (2002)

Colossal Reversible Volume Changes in Li Alloys

Intercalation of atoms or ions into solid lattices is fundamental to the behavior of many of the electrode materials used in advanced batteries. Some examples include hydrogen in metal hydrides and lithium in carbon, metal oxides, and lithium alloys. Researchers from Dalhousie University and the 3M Company have studied volume changes in lithium alloys, using *in situ* optical and atomic force microscopy, during electrochemical intercalation of lithium into sputtered films. The films expand perpendicular to the substrate when lithium is first intercalated; upon Li removal, they shrink in both parallel and perpendicular directions resulting in the formation of large (on the order of 100 μm) cracks. Subsequent intercalation results in the cracks seemingly disappear as the lattice expands. Further cycles reveal that these large volume changes occur reversibly. Optical and AFM images, taken at various points during a large number of charge and discharge cycles, revealed this interesting behavior, which the authors compare qualitatively to the desiccation of mud in a lake bed. Time-lapsed movies, posted at www.physics.dal.ca/~dahn/ECS_Letters.html, provide a window to the usefulness of this *in situ* technique. The ability to understand and control lithium intercalation provides a controlled framework for studying the effects of strains, volume changes, and fractures on the performance of these important alloys.

From: *Electrochem. Solid-State Lett.*, 4, A137 (2001)

High Performance Anodes for Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) provide one option for meeting society's ever-increasing energy needs. To further their general utility in this regard, as well as to increase efficiencies and reduce costs, there has been a significant level of research focused on lowering the operating temperature of these devices. Researchers at Nagoya University and the National Institute of Advanced Industrial Science and Technology in Japan have reported a study on high performance anodes for SOFCs operating in methane-air mixtures at reduced temperatures. The anodes were NiO-samarium cermet doped with various levels of PtO₂, PdO, Rh₂O₃, or RuO₂, with the best performance being observed with the PdO doped material. In fact, very little if any enhancement was observed with any of the other dopants. A range of PdO concentrations were evaluated, and the highest activity was observed at a concentration of 7 wt %, corresponding to a catalyst loading of 0.145 mg/cm². Using the optimum anode formulation, a Ce_{0.8}Sm_{0.2}O_{1.9} electrolyte thickness of 0.15 mm, and methane-air mixtures, the highest power observed for this SOFC was 644 mW/cm² at 550°C, with an open circuit voltage of approximately 900 mV. The authors do point out that various issues still need to be addressed, such as the low fuel utilization which is only 9.4% at the highest power levels observed.

From: *J. Electrochem. Soc.*, 149, A133 (2002)

Tech Highlights was prepared by Zenghe Liu of TheraSense, Inc., Venkat Srinivasan of The University of California, Berkeley, and Terry Guilinger, David Ingersoll, and Mike Kelly of Sandia National Laboratories.